

DECLARATION

I, Chizuko IKEDA, declare that I reside at 5-50-301,
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That I am familiar with the English and Japanese
languages;

That I have prepared a translation of Japanese Patent
Application No. 2003-361801, "接合用樹脂組成物, JOINABLE RESIN
COMPOSITION"; said translation thereof being attached hereto
and made a part of this declaration;

That to the best of my knowledge and belief, the attached
translation is accurate and fairly reflects the contents and
meaning of the foregoing Japanese language document.

I declare, under penalty of perjury under the laws of
the United States of America, that the foregoing is true and
correct.

Executed, on November 15, 2011.

A handwritten signature in cursive script, reading "Chizuko Ikeda", is written over a horizontal line.

Chizuko IKEDA

JAPAN PATENT OFFICE

This is to certify that the annexed is a true copy
of the following application as filed with this Office.

Date of Application: October 22, 2003

Application Number: 2003-361801

[ST.10/C] [JP2003-361801]

Applicant(s): Daicel-Degussa Ltd.

October 28, 2004

Commissioner,

Japan Patent Office

Hiroshi OGAWA

Certification No. 2004-3097777

[Document Name]	Petition for Patent
[Docket No.]	P030103
[Filing Date]	October 22, 2003
[Address]	Commissioner, Patent Office
[International Patent Classification]	C09J 5/00
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[Payment of Fees]		
[Payment Book No.]	009829	
[Amount to be paid]	¥21,000	
[Attached Documents]		
[Item]	Claims	one copy
[Item]	Description	one copy
[Item]	Abstract	one copy
[Identification No. of General Power]	9707828	

[Document Name] Claims

[Claim 1]

A resin composition directly joinable to a thermoplastic urethane-series resin, which comprises a
5 non-urethane-series thermoplastic resin and an amino group-containing compound.

[Claim 2]

A resin composition according to Claim 1, which contains an amino group in a concentration of not less than
10 10 mmol/kg.

[Claim 3]

A resin composition according to Claim 1, wherein the non-urethane-series thermoplastic resin comprises at least one member selected from the group consisting of a
15 polyamide-series resin, a polyester-series resin, a polycarbonate-series resin, a polyphenylene sulfide-series resin, a polysulfone-series resin, a thermoplastic polyimide-series resin, a polyetherketone-series resin, an olefinic resin, a styrenic
20 resin, a (meth)acrylic resin, and a halogen-containing vinyl-series resin.

[Claim 4]

A resin composition according to Claim 1, wherein the amino group-containing compound has a plurality of
25 primary amino groups in the molecule.

[Claim 5]

A resin composition according to Claim 1, wherein

the amino group-containing compound has an amino group in a concentration of 40 to 1000 mmol/kg.

[Claim 6]

A resin composition according to Claim 1, wherein
5 the amino group-containing compound is a polyamide oligomer having a number average molecular weight of 500 to 10,000 and an amino group in a concentration of 50 to 700 mmol/kg.

[Claim 7]

A resin composition according to Claim 1, wherein
10 the proportion of the amino group-containing compound is 0.01 to 20 parts by weight relative to 100 parts by weight of the non-urethane-series thermoplastic resin.

[Claim 8]

A resin composition according to Claim 1, which
15 comprises

a polyamide oligomer; and

at least one non-urethane-series thermoplastic resin selected from the group consisting of a polyamide-series resin, a polyester-series resin, a polycarbonate-series
20 resin and a polyphenylenesulfide-series resin.

[Claim 9]

A molded composite article in which a resin member comprising a non-urethane-series thermoplastic resin composition and a resin member comprising a thermoplastic
25 polyurethane-series resin are directly joined with each other, wherein the non-urethane-series thermoplastic resin composition comprises a non-urethane-series thermoplastic

resin and an amino group-containing compound.

[Claim 10]

A process for producing a molded composite article
recited in Claim 9, which comprises

5 heating at least one resin selected from the group
consisting of the non-urethane-series thermoplastic resin
composition and the thermoplastic polyurethane-series
resin, and

 joining the resin composition and the resin with each
10 other.

[Document Name] Description

[Title of the Invention] JOINABLE RESIN COMPOSITION

[Technical Field]

[0001]

5 The present invention relates to a joinable or bondable resin composition suitable for joining to a resin member comprising a thermoplastic polyurethane in a one-piece construction without an adhesive.

[Background Art]

10 [0002]

 In order to improve design or decorative property, or in order to impart excellent touch or texture (e.g., soft texture), there have been proposed composites (molded composite articles) formed with a combination of a plurality of resins each having a different hardness, for example, a molded composite article in which at least a part of a resin molded article is coated with a thermoplastic elastomer. Such a molded composite article is usually produced by adhesion of a plurality of molded members through an adhesive. For example, Japanese Patent Application Laid-Open No. 267585/1996 (JP-8-267585A) (Patent Document 1) discloses a resin molded article in which a plurality of resin molded articles formed with a polyamide resin or others are welded or adhered to each other through a finishing agent such as a urethane polymer or a urethane-series adhesive. However, such a process using an adhesive is not only uneconomical due to complicated steps, but also has

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problems such as environmental pollution by an organic solvent or others.

[0003]

On the other hand, from the viewpoint of
5 rationalization of production processes or environmental protection, a process for thermal fusing of a plurality of molded members has been adopted. The molded composite article obtained by thermal fusing is usually manufactured by a molding process such as a two-color (or double) molding
10 or an insert injection molding. However, combination of materials which are different in species and are acceptable for thermal fusing is significantly limited. Moreover, it is not easy to establish molding conditions for obtaining enough bonded strength. Therefore, in order to reinforce
15 the fused part, such a method is utilized in addition to thermal fusing or welding, that a method for preparing a concavo-convex site (or part) in an area to be bonded of the molded member for mechanical joining, a method for coating a primer or others on an area to be bonded, or other
20 methods. In such a method, however, the molded composite article is deteriorated in flexuous property. For example, the hardened primer layer easily forms a crack with bending. Moreover, the method tends to require a complicated structure of the molded member, or increases the number
25 of production steps.

[0004]

In order to solve these problems, it has been

investigated to use a thermoplastic polyurethane as a material for a resin member constituting a molded composite article. The thermoplastic polyurethane itself is relatively excellent in adhesiveness. For example, in a
5 usage(or purpose) of shoe(s), a molded composite plastic article comprising a polyamide resin and a thermoplastic polyurethane is practically used as a shoe sole. Moreover, Japanese Patent Application Laid-Open No. 505333/1996 (JP-8-505333A) (Patent Document 2) discloses that a
10 lightened shoe sole is obtained by injection-molding a polyamide elastomer containing a foaming agent into a mold, with inserting or putting a molded article of a thermoplastic resin such as a polyether amide, a polyether ester or a polyurethane in a mold, and adhering to the thermoplastic
15 resin molded article (un-lightweight (un-lightened) plastic) and the elastomer (lightweight thermoplastic elastomer). Japanese Patent Application Laid-Open No. 125155/1995 (JP-7-125155A) (Patent Document 3) discloses a molded composite article in which a rigid plastic molded
20 member formed of a blended matter of a polypropylene and a polyamide is coated with a non-rigid (or flexible) plastic containing a thermoplastic polyurethane and a plasticizer by thermal fusing. However, even in such a molded composite article (for example, a molded composite article using a
25 polyurethane resin), the adhesive strength between two materials (e.g., an adhesive strength relative to a polyamide elastomer as a counterpart member) has not been

enough yet. Therefore, such a composite is affected by not only conditions for molding or conditions of materials to be used (e.g., production lot) but also using environment of the product (molded composite article), resulting in
5 unstableness of the bonded strength (or joined strength) or the duration of the molded composite article (particularly the duration of the adhered site).

[Patent Document 1] JP-8-267585A (Claims)

[Patent Document 2] JP-8-50533A (Claims)

10 [Patent Document 3] JP-7-125155A (Claims)

[Disclosure of the Invention]

[Problems to be Solved by the Invention]

[0005]

It is therefore an object of the present invention
15 to provide a resin composition firmly joinable or bondable to a thermoplastic urethane-series resin member without an adhesive regardless of comprising a non-urethane-series thermoplastic resin as a base resin.

[0006]

20 It is another object of the present invention to provide a resin composition improving joinability (or joining property) to a thermoplastic urethane-series resin member independent of the kinds of base resin.

[0007]

25 It is still another object of the present invention to provide a resin composition firmly joinable to a thermoplastic urethane-series resin member without

deteriorating base resin properties.

[0008]

It is a further object of the present invention to provide a molded composite article in which, even using
5 a non-urethane-series resin member and a thermoplastic polyurethane-series resin member different in character from each other, the both members are directly and firmly joined together without an adhesive; and a process for producing the same.

10 [0009]

It is another object of the present invention to provide a process for producing a molded composite article in which a non-urethane-series resin member and a thermoplastic polyurethane-series resin member are firmly
15 joined together by thermal fusing in a convenient manner without going through complicated production steps.

[Means to Solve the Problems]

[0010]

The inventors of the present invention made intensive
20 studies to achieve the above objects and finally found that a resin composition containing a non-urethane-series thermoplastic resin as a base resin and an amino group-containing compound shows high joinability to a thermoplastic polyurethane-series resin, thereby a resin
25 member comprising the resin composition and a resin member comprising the thermoplastic polyurethane-series resin are firmly bonded or joined with each other. The present

invention was accomplished based on the above findings.

[0011]

That is, the joinable resin composition of the present invention is a resin composition (non-urethane-series resin composition) directly joinable to a thermoplastic urethane-series resin, and the resin composition comprises a non-urethane-series thermoplastic resin and an amino group-containing compound. The resin composition may have an amino group in a concentration of not less than 10 mmol/kg.

10 The non-urethane-series thermoplastic resin may comprise at least one member selected from the group consisting of a polyamide-series resin, a polyester-series resin, a polycarbonate-series resin, a polyphenylene sulfide-series resin, a polysulfone-series resin, a

15 thermoplastic polyimide-series resin, a polyetherketone-series resin, an olefinic resin, a styrenic resin, a (meth)acrylic resin, and a halogen-containing vinyl-series resin. The amino group-containing compound may have a plurality of primary amino groups in the molecule.

20 The amino group-containing compound may have an amino group in a concentration of 40 to 1000 mmol/kg. The amino group-containing compound may be a polyamide oligomer having a number average molecular weight of 500 to 10,000 and an amino group in a concentration of 50 to 700 mmol/kg. The

25 proportion of the amino group-containing compound may be about 0.01 to 20 parts by weight relative to 100 parts by weight of the non-urethane-series thermoplastic resin.

The resin composition may contain a non-urethane-series thermoplastic resin selected from the group consisting of a polyamide-series resin, a polyester-series resin, a polycarbonate resin and a polyphenylene sulfide-series resin; and a polyamide oligomer.

[0012]

The present invention also includes a molded composite article in which a resin member comprising a non-urethane-series resin composition and a resin member comprising a thermoplastic polyurethane-series resin are directly joined with each other, wherein the non-urethane-series resin composition comprises a non-urethane-series thermoplastic resin and an amino group-containing compound. Moreover, the present invention includes a process for producing the molded composite article, which comprises heating at least one resin selected from the group consisting of the non-urethane-series resin composition and the thermoplastic polyurethane-series resin, and joining the resin composition and the resin with each other.

[0013]

Incidentally, throughout this specification, the meaning of the term "resin" sometimes includes "a resin composition". Moreover, throughout this specification, the term "adhesion (or adhering)" means a technique for compounding a plurality of members through an adhesive, the term "joining (or bonding)" means a technique for

compounding a plurality of members without an adhesive,
and the both terms are distinguished from each other. Fusing
(or thermal fusing) is one embodiment of joining.

[Effects of the Invention]

5 [0014]

Since the resin composition of the present invention
comprises a non-urethane-series thermoplastic resin and
an amino group-containing compound, in spite of using a
non-urethane-series thermoplastic resin as a base resin,
10 the non-urethane-series thermoplastic resin composition
can be firmly or strongly joined or bonded to a thermoplastic
urethane-series resin member without an adhesive.
Moreover, an amino group-containing compound achieves
improvement in joinability of the non-urethane-series
15 thermoplastic resin to the thermoplastic urethane-series
resin member regardless of the species of the base resin.
Furthermore, in the case where the resin composition
contains a polyamide oligomer, without deteriorating
properties of the base resin, the resin composition can
20 be firmly joined to the thermoplastic urethane-series resin
member. In the molded composite article of the present
invention, combination of the above-mentioned resin
composition and the thermoplastic polyurethane-series
resin ensures direct and strong bonding or joining of the
25 non-urethane-series resin member with the thermoplastic
polyurethane-series resin member without an adhesive,
regardless of the different properties of the above resin

members. Moreover, according to the process of the present invention, a molded composite article is producible in which a non-urethane-series resin member and a thermoplastic polyurethane resin member are firmly joined together by thermal fusing in a simple manner without going through complicated production steps.

[Preferred Embodiment of the Invention]

[0015]

[Resin composition]

10 The resin composition of the present invention comprises a base resin (non-urethane-series thermoplastic resin) and an amino group-containing compound, and is suitable for forming or shaping a molded composite article (composite molded article) by joining or bonding to a thermoplastic urethane-series resin.

[0016]

(Base resin)

As the non-urethane-series thermoplastic resin being a base resin of the resin composition, for example, there may be exemplified that a polyamide-series resin, a polyester-series resin, a polycarbonate-series resin, a polyphenylene sulfide-series resin, a polysulfone-series resin [e.g., a polysulfone, a poly(ether sulfone), and a poly(4,4'-bisphenoether sulfone)], a thermoplastic polyimide-series resin, a polyether ketone-series resin [e.g., a polyether ketone, a poly(ether-ether ketone)], an olefinic resin, a styrenic resin, a (meth)acrylic resin,

a halogen-containing vinyl-series resin, and others.
These non-urethane-series thermoplastic resins can be used
singly or in combination.

[0017]

5 (1) Polyamide-series resin

As the polyamide-series resin, there may be mentioned
an aliphatic polyamide-series resin, an alicyclic
polyamide-series resin, an aromatic polyamide-series resin,
or others, and various homopolyamides and copolyamides may
10 be used.

[0018]

Among the aliphatic polyamide-series resins, the
homopolyamide may include a condensation product of an
aliphatic diamine component [e.g., a C₄₋₁₆alkylenediamine
15 such as tetramethylenediamine, hexamethylenediamine, or
dodecanediamine (preferably a C₄₋₁₄alkylenediamine,
particularly a C₆₋₁₂alkylenediamine)] and an aliphatic
dicarboxylic acid component [e.g., an alkylenedicarboxylic
acid having about 4 to 20 carbon atoms, such as adipic acid,
20 sebacic acid, or dodecanedioic acid (preferably a
C₄₋₁₆alkylenedicarboxylic acid, and particularly a
C₆₋₁₄alkylenedicarboxylic acid)], for example, a polyamide
46, a polyamide 66, a polyamide 610, a polyamide 612, and
a polyamide 1010; a homopolyamide of a lactam [e.g., a lactam
25 having about 4 to 20 (preferably about 4 to 16) carbon atoms,
such as ϵ -caprolactam or ω -laurolactam] or an
aminocarboxylic acid [e.g., an aminocarboxylic acid having

about 4 to 20 (preferably about 4 to 16) carbon atoms, such as ω -aminoundecanoic acid], for example, a polyamide 6, a polyamide 11, and a polyamide 12; and others. Moreover, the copolyamide may include a copolyamide which can be
5 obtained by copolymerization of a monomer component capable of constituting a polyamide, e.g., the aliphatic diamine components, the aliphatic dicarboxylic acid components, the lactams and the aminocarboxylic acids. Examples of the copolyamide may include a copolymer of 6-aminocaproic acid
10 and 12-aminododecanoic acid; a copolymer of 6-aminocaproic acid, 12-aminododecanoic acid, hexamethylenediamine and adipic acid; a copolymer of hexamethylenediamine, adipic acid, hydrogenated dimer acid and 12-aminododecanoic acid; a polyamide 6/11, a polyamide 6/12, a polyamide 66/11, a
15 polyamide 66/12; and others.

[0019]

The alicyclic polyamide-series resin may include a homopolyamide or copolyamide having at least one component selected from the group consisting of at least an alicyclic
20 diamine and an alicyclic dicarboxylic acid as a constitutive component. As such an alicyclic polyamide-series resin, for example, there may be used an alicyclic polyamide obtained by using an alicyclic diamine and/or an alicyclic dicarboxylic acid as at least one component among a diamine
25 component and a dicarboxylic acid component each constituting a polyamide-series resin. As the diamine component and the dicarboxylic acid component, the

above-mentioned aliphatic diamine(s) and/or aliphatic dicarboxylic acid(s) are preferably used in combination with the alicyclic diamine(s) and/or alicyclic dicarboxylic acid(s). Such an alicyclic polyamide-series resin has a high transparency and is known as what is called transparent polyamide.

[0020]

Examples of the alicyclic diamine may include a diaminocycloalkane such as diaminocyclohexane (e.g., a diaminoC₅₋₁₀cycloalkane); a bis(aminocycloalkyl)alkane such as bis(4-aminocyclohexyl)methane, bis(4-amino-3-methylcyclohexyl)methane, or 2,2-bis(4'-aminocyclohexyl)propane [e.g., a bis(aminoC₅₋₈cycloalkyl)C₁₋₃alkane]; and others. Moreover, the alicyclic dicarboxylic acid may include a cycloalkanedicarboxylic acid such as cyclohexane-1,4-dicarboxylic acid or cyclohexane-1,3-dicarboxylic acid (for example, a C₅₋₁₀cycloalkane-dicarboxylic acid), and others.

[0021]

Among the alicyclic polyamide-series resins, for example, a condensation product (a homo- or copolyamide) of the aliphatic dicarboxylic acid and the alicyclic diamine is preferred.

[0022]

The aromatic polyamide-series resin may include a polyamide in which at least one component selected from

the aliphatic diamine component and the aliphatic dicarboxylic acid component comprises an aromatic component, for example, a polyamide having an aromatic component in a diamine component [for example, a condensation product
5 of an aromatic diamine (e.g., metaxylylenediamine) and an aliphatic dicarboxylic acid, such as MXD-6], a polyamide having an aromatic component in a dicarboxylic acid component [e.g., a condensation product of an aliphatic diamine (e.g., trimethylhexamethylenediamine) and an
10 aromatic dicarboxylic acid (e.g., terephthalic acid, isophthalic acid)], and others.

[0023]

Incidentally, in the polyamide-series resin, a polyamide in which both a diamine component and a
15 dicarboxylic acid component comprise an aromatic component [for example, a perfect aromatic amide such as a poly(m-phenyleneisophthalamide) (e.g., Aramid)] may be used in combination.

[0024]

20 The polyamide-series resin may further include a polyamide comprising a dimer acid as a dicarboxylic acid component, a polyamide in which a branched chain structure is introduced by using a small amount of a polyfunctional polyamine and/or polycarboxylic acid component, a modified
25 polyamide (e.g., a N-alkoxymethylpolyamide), a polyamide block copolymer, and others.

[0025]

Examples of the polyamide block copolymer may include a polyamide elastomer such as a polyamide-polyether block copolymer (e.g., a polyamide-polyether block copolymer containing a polyether segment or block such as a
5 polytetramethylene glycol, a polyethylene glycol, or a polypropylene glycol as a soft segment). The polyamide-polyether block copolymer may include a block copolymer obtained by copolycondensation of a polyamide block having a reactive terminal group and a polyether block
10 having a reactive terminal (terminal group), particularly, a polyether amide (e.g., a block copolymer of a polyamide block having diamine terminals with a polyoxyalkylene block having dicarboxyl terminals, a block copolymer of a
15 polyamide block having dicarboxyl terminals with a polyoxyalkylene block having diamine terminals), a polyether ester amide (e.g., a block copolymer of a polyamide block having dicarboxyl terminals with a polyoxyalkylene block having dihydroxy terminals), and others.
Incidentally, commercially available polyamide elastomers
20 usually scarcely have amino groups in many cases.

[0026]

The polyamide-series resin may be used singly or in combination. Moreover, the polyamide-series resin may be a blend or alloy of a plurality of polyamide-series resins.

25 [0027]

The preferred polyamide-series resin includes an aliphatic polyamide-series resin, an alicyclic

polyamide-series resin (particularly, a transparent polyamide), and others. The polyamide-series resin may be used in combination with an aromatic polyamide-series resin in combination. Furthermore, the polyamide block
5 copolymer is also preferred.

[0028]

The number average molecular weight of the polyamide-series resin is about 6,000 to 100,000, preferably about 8,000 to 50,000, and more preferably about 10,000
10 to 30,000.

[0029]

Incidentally, in the case where a polyamide-series resin is used as the base resin, in order to enhance joinability of a non-urethane-series thermoplastic resin member (e.g., a hard resin member) with a thermoplastic
15 polyurethane-series resin member (e.g., a soft resin member), the enthalpies of fusion and crystallization of the polyamide-series resin may be not more than 100 J/g (e.g., about 0 to 100 J/g), preferably not more than 80 J/g (e.g.,
20 about 0 to 80 J/g), and more preferably not more than 70 J/g (e.g., about 0 to 70 J/g). According to the present invention, even using a polyamide-series resin having a low degree of crystallinity, certain and efficient joining can be ensured. The enthalpies of fusion and
25 crystallization in such a polyamide-series resin may for example be selected from a range of not more than 30 J/g (e.g., about 0 to 30 J/g), preferably not more than 20 J/g

(e.g., about 0 to 20 J/g), and more preferably not more than 17 J/g (about 0 to 17 J/g).

[0030]

The "enthalpies of fusion and crystallization" of
5 the polyamide-series resin means a value obtained by
subtracting a heat of crystallization (ΔH_f) generated along
with crystallization of a resin from a heat of fusion (ΔH_m)
necessary to melt the resin. That is, in a measurement of
the heat of fusion, if both the heat of crystallization
10 and the following heat of fusion are observed along with
raising the temperature, the enthalpies of fusion and
crystallization of the polyamide-series resin is assessed
as a value subtracted the found value ΔH_f of the heat of
crystallization per one gram of the resin from the found
15 value ΔH_m of the heat of fusion per one gram of the resin.
The enthalpies of fusion and crystallization can be measured
by a differential scanning calorimeter (DSC apparatus) based
on JIS (Japanese Industrial Standards) K 7122.
Incidentally, since the heat of crystallization cannot be
20 observed in a perfect amorphous polyamide, the enthalpies
of fusion and crystallization of such a polyamide is
qualified as 0 J/g.

[0031]

The polyamide-series resin having such enthalpies
25 of fusion and crystallization, in particular a
polyamide-series resin having enthalpies of fusion and
crystallization of not more than 20 J/g (e.g., a transparent

polyamide) may be molded by a known molding method. The further details about of such a polyamide-series resin may for example be referred to Japanese Patent Application Laid-Open No. 239469/1996 (JP-8-239469A), Japanese Patent
5 Application Laid-Open No. 1544/2000 (JP-2000-1544A), and others.

[0032]

Incidentally, the concentration of the carboxyl group (or carboxyl group concentration) in the polyamide-series
10 resin is not particularly limited to a specific one, and may for example be about 0.1 to 200 mmol/kg, preferably about 0.5 to 150 mmol/kg, and more preferably about 1 to 100 mmol/kg.

[0033]

15 (2) Polyester-series resin

The polyester-series resin may include a polyalkylene arylate (e.g., a C₂₋₄alkylene terephthalate such as a polyethylene terephthalate or a polybutylene terephthalate, and a C₂₋₄alkylene naphthalate such as a polyethylene
20 naphthalate, or the copolyester thereof [e.g., a copolyester which comprises a diol component (e.g., a (poly)oxyC₂₋₄alkylene glycol such as ethylene glycol, or a polyethylene glycol; an aliphatic C₅₋₁₆diol such as 1,6-hexanediol; an alicyclic diol such as 1,4-cyclohexane
25 dimethanol), and a dicarboxylic acid component (e.g., an aliphatic dicarboxylic acid such as adipic acid or sebacic acid; and an aromatic dicarboxylic acid such as isophthalic

acid) as a copolymerizable component], a polyester-series elastomer [e.g., a polyester-polyether-based polyester elastomer which comprises a polyC₂₋₄alkylene arylate such as a polyethylene terephthalate or a polybutylene terephthalate as a hard segment, a polyoxyC₂₋₄alkylene glycol such as a polytetramethylene glycol as a soft segment; and a polyester-polyester-based polyester elastomer which comprises the polyC₂₋₄alkylene arylate as a hard segment and a polyaliphatic ester such as a poly(ϵ -caprolactone) or a polybutylene adipate as a soft segment], and others.

[0034]

(3) Polycarbonate-series resin

The polycarbonate-series resin may include a polymer obtained by reaction of a dihydroxy compound [e.g., an alicyclic diol or a bisphenol compound (e.g., a bis(hydroxyaryl)C₁₋₆alkane such as bis(4-hydroxyphenyl)methane or bisphenol A, in addition, 4,4'-dihydroxydiphenylether, 4,4'-dihydroxydiphenylsulfone, 4,4'-dihydroxydiphenylsulfide, and 4,4'-dihydroxydiphenylketone)] with phosgene or a carbonic acid ester (e.g., diphenyl carbonate), and others.

[0035]

(4) Polyphenylene sulfide-series resin

The polyphenylene sulfide-series resin includes a linear or crosslinked polyphenylene sulfide, and others.

[0036]

(5) Olefinic resin

The olefinic resin (or polyolefinic resin) may include a homo- or copolymer of a C₂₋₁₀olefine (e.g., a polyethylene, a polypropylene, a poly(1-butene), and an
5 ethylene-propylene copolymer), a copolymer of an olefin with a copolymerizable monomer (e.g., an ethylene-vinyl acetate copolymer, an ethylene-(meth)acrylate copolymer), a modified polyolefin], a polyolefinic elastomer (an elastomer containing a hard segment comprising a polyolefin
10 (such as a polyethylene or a polypropylene) and a soft segment comprising a rubber component (such as an ethylene-propylene rubber (EPR) or an ethylene-propylene-diene rubber (EPDM)), and others.

[0037]

15 (6) Styrenic resin

The styrenic resin may include a polystyrene (GPPS), a high impact polystyrene (HIPS), an acrylonitrile-styrene copolymer (AS resin), an acrylonitrile-butadiene-styrene block copolymer (ABS resin), a polystyrenic elastomer (e.g.,
20 a styrene-butadiene-styrene (SBS) block copolymer, a styrene isoprene-styrene (SIS) block copolymer) and others.

[0038]

(7) (Meth)acrylic resin

The (meth)acrylic resin may include a homo- or
25 copolymer of a (meth)acrylic acid or an ester thereof [e.g., a poly(methyl methacrylate)], a copolymer of (meth)acrylic acid or an ester thereof with other copolymerizable monomer

[e.g., a (meth)acrylic acid-styrene copolymer, and a methyl methacrylate-styrene copolymer], and others.

[0039]

(8) Halogen-containing vinyl-series resin

5 The halogen-containing vinyl-series resin may include a chlorine-containing vinyl-series resin such as a poly(vinyl chloride), a vinyl chloride-vinyl acetate copolymer, a fluorine-containing vinyl-series resin, a poly(vinyl chloride)-series elastomer, a fluorine-series
10 thermoplastic elastomer, and others.

[0040]

 The non-urethane-series thermoplastic resin can be used singly or in combination. Among the non-urethane-series thermoplastic resins, a
15 polyamide-series resin, a polyester-series resin, a polycarbonate-series resin, a polyphenylene sulfide-series resin, a polystyrenic resin, polyolefinic resin and others are preferred. Moreover, as the non-urethane-series thermoplastic resin, a thermoplastic
20 elastomer (e.g., a polyamide-series elastomer, a polyester-series elastomer, a polyolefinic elastomer, a polystyrenic elastomer, a poly(vinyl chloride)-series elastomer, and a fluorine-containing thermoplastic elastomer) may be employed.

25 [0041]

 The base resin may have or substantially may not have an amino group. In the case where the base resin has an

amino group, the base resin may have an amino group in a side chain of the resin or at the end of a main chain thereof. Incidentally, the amino group usually means a free amino group (-NH₂ group), and usually does not include an amide bond included in a main chain of the base resin (e.g., a
5 polyamide-series resin), a urea bond, a -NH- (imino) group and a -N< group derived from a urethane bond.

[0042]

The content (or concentration) of amino group in the
10 base resin may be small, for example, about 0 to 20 mmol/kg, preferably about 0 to 10 mmol/kg, and more preferably about 0 to 8 mmol/kg.

[0043]

(Amino group-containing compound)

15 As the amino group-containing compound, there may be used various amino group-containing compounds which are mixable with the base resin, such as a polyamine [e.g., a diamine (for example, the above-mentioned aliphatic diamines, alicyclic diamines and aromatic diamines); in
20 addition, a polyamine, for example, an aliphatic polyamine such as a polyalkylenepolyamine such as diethylenetriamine, or triethylenetetramine (e.g., a polyC₂-3alkylenepolyamine)], a monoamine, and a polyamide oligomer.

25 [0044]

As the polyamide oligomer, there may be used a polyamide having a relatively low molecular weight, which

is obtained by a conventional manner, for example, by adjusting polycondensation or other conditions and using the above-mentioned polyamide component(s). For example, as a polyamide component to be a raw material, there may be mentioned the combination of the above-mentioned diamine [e.g., an aliphatic diamine (e.g., an alkylenediamine), an alicyclic diamine, and an aromatic diamine] and a dicarboxylic acid (e.g., an aliphatic dicarboxylic acid, and an aromatic dicarboxylic acid), the combination of the above-mentioned diamine and/or dicarboxylic acid and the lactam (e.g., a lactam having about 4 to 20 carbon atoms, such as ω -laurolactam), and other combinations. The polyamide oligomer may be obtained by for example polymerizing the lactam and the aliphatic diamine with heating and stirring under an applied pressure.

[0045]

The number average molecular weight of the polyamide oligomer is, for example, about 500 to 10,000, preferably about 500 to 8,000 (e.g., about 1,000 to 7,000), more preferably about 1,000 to 5,000, and usually about 2,000 to 6,000 (e.g., about 3,000 to 6,000). As the polyamide oligomer, for example, the number average molecular weight may be about 1000 to 10,000, preferably about 2,000 to 9,000, and more preferably about 3,000 to 8,000. Use of such a polyamide oligomer improves the joinability (or joining property) of the polyamide-series resin constituting the resin member to the thermoplastic polyurethane.

[0046]

The polyamide oligomer may usually have a free amino group at least at one terminal of the main chain, may have free amino groups at both terminals of the main chain, or
5 may have a free amino group at a side chain. The amino group-containing compound can be used singly or in combination.

[0047]

The amino group-containing compound may be a monoamine,
10 and is usually preferred to be a compound having not less than two amino groups (e.g., primary amino group) in a molecule, particularly, to be a polyamide oligomer in terms of joinability.

[0048]

15 The amino group concentration of the amino group-containing compound may for example be about 40 to 1000 mmol/kg, preferably about 50 to 700 mmol/kg, and more preferably about 100 to 500 mmol/kg. In particular, the amino group-containing compound preferably has a terminal
20 amino group in the above range.

[0049]

The proportion of the amino group-containing compound, relative to 100 parts by weight of the base resin, can for example be selected from the range of about 0.01 to 20 parts
25 by weight, and may be preferably not more than 10 parts by weight (about 0.01 to 10 parts by weight), more preferably about 0.1 to 8 parts by weight, and particularly not more

than 7 parts by weight (about 0.5 to 7 parts by weight).
Incidentally, excess amount of the amino group-containing
compound may deteriorate the resin property, particularly
in the case of using a non-urethane-series thermoplastic
5 resin composition as a hard resin.

[0050]

Since the resin composition of the present invention
usually contains an amino group (usually, an amino group
derived from the amino group-containing compound), the resin
10 composition can directly and firmly join or bond with a
thermoplastic polyurethane-series resin or resin member.
The proportion (or concentration) of amino group in the
resin composition may for example be not less than 10 mmol
(e.g., about 10 to 300 mmol), preferably not less than 15
15 mmol (e.g., about 15 to 200 mmol), about not less than 20
mmol (e.g., about 20 to 150 mmol), and particularly not less
than 30 mmol (e.g., about 30 to 100 mmol) in 1 kg of the
resin composition. In particular, the resin composition
preferably has a terminal amino group in such a range.
20 Incidentally, the amino group concentration in the resin
composition is suitably adjustable with the amino group
concentration in the non-urethane-series thermoplastic
resin or the amino group-containing compound, or the
proportion of these components.

25 [0051]

Incidentally, in the case of producing a molded
composite article by joining a non-urethane-series

thermoplastic resin composition with a thermoplastic
polyurethane-series resin, a "warp" in the product sometimes
occurs in association with joining due to the difference
between mold shrinkage factors of the resin members. In
5 particular, in the case where the degree of the correction
for the warp is large, there is a possibility that breaking
of the joining part or generation of stress crack in each
resin member occurs. Therefore, the non-urethane-series
thermoplastic resin (e.g., the polyamide-series resin)
10 preferably has lower crystallinity.

[0052]

For example, the final crystallinity degree (mean
final crystallinity degree) of the polyamide-series resin
is advantageously not more than 50% (e.g., about 5 to 50%),
15 preferably not more than 40% (e.g., about 5 to 40%), and
more preferably not more than 30% (e.g., about 10 to 30%).
In the case where a polyamide homopolymer is taken as an
example and the final crystallinity degree is compared,
the final crystallinity degree becomes smaller in the
20 following order:

[0053]

polyamide 66 > polyamide 6 ≥ polyamide 612 > polyamide
11 ≥ polyamide 12

Incidentally, considering only the final
25 crystallinity degree, the copolymer is more advantageous
than the homopolymer. Further, in general the copolymer
is also more advantageous than the homopolymer from the

perspective that the copolymer is superior to the homopolymer in flexibility.

[0054]

In the case of a polyamide block copolymer (a polyamide elastomer) which comprises a polyamide homopolymer as a hard segment and a polyether as a soft segment, the final crystallinity degree can be adjusted by the ratio of the hard segment and the soft segment. When the final crystallinity degree of the polyamide block copolymer is adjusted to not more than 40% (e.g., about 5 to 40%), preferably not more than 35% (e.g., about 5 to 35%) and more preferably not more than 30% (e.g., about 10 to 30%), such a copolymer is advantageously used in combination with a thermoplastic polyurethane-series resin member for inhibiting warp generation, and further can provide a flexibility which suits with that of a thermoplastic polyurethane-series resin.

[0055]

Incidentally, the term "the final crystallinity degree" means a degree of crystallinity measured by an X-ray diffraction analysis using a flat plate 1 mm thick, where the flat plate is formed by heating a sample resin to a temperature which is 20°C higher than a melting point thereof, and then cooling the resin to a room temperature at a rate of 3°C/minute by means of a precision (or accurate) heat pressing machine. The melting point of the resin is measured by a differential scanning calorimeter (DSC apparatus) in

accordance with JIS K 7122.

[0056]

In such a range that the effects of the present invention are not deteriorated, the resin composition may
5 contain other resins, and various additives, for example, a filler or reinforcing agent (e.g., a reinforcing fiber), a stabilizer (e.g., a ultraviolet ray absorbing agent, an antioxidant, and a heat stabilizer), a coloring agent, a plasticizer, a lubricant, a flame retardant, an antistatic
10 agent, and others.

[0057]

Since such a resin composition contains an amino group, in spite of using a non-urethane-series thermoplastic resin as a base resin, the resin composition can be directly and
15 firmly joined or bonded to a polyurethane-series resin (including a resin member).

[0058]

[Molded composite article]

The molded composite article can be produced by
20 joining (or bonding) the non-urethane-series thermoplastic resin composition with the thermoplastic polyurethane-series resin under heating.

[0059]

(Polyurethane-series resin)

25 The polyurethane-series resin joinable with the non-urethane-series thermoplastic resin composition may include a polyurethane-series resin obtainable by reacting

a diisocyanate, a diol and, if necessary, a chain-extension agent.

[0060]

The diisocyanate may include an aliphatic
5 diisocyanate such as hexamethylene diisocyanate (HMDI),
or 2,2,4-trimethylhexamethylene diisocyanate; an
alicyclic diisocyanate such as 1,4-cyclohexane
diisocyanate, a dicycloalkylmethane-4,4'-diisocyanate, or
isophorone diisocyanate (IPDI); an aromatic diisocyanate
10 such as phenylene diisocyanate, tolylene diisocyanate (TDI),
or diphenylmethane-4,4'-diisocyanate (MDI); an
araliphatic diisocyanate such as xylylene diisocyanate;
and others. As the diisocyanate, there may also be used
a compound having an alkyl group (e.g., methyl group)
15 substituted on a main chain or ring thereof. The
diisocyanate(s) may be used singly or in combination.

[0061]

Examples of the diol may include a polyester diol
[for example, a polyester diol (aliphatic polyester diol)
20 derived from an aliphatic dicarboxylic acid component (e.g.,
a C₄₋₁₂ aliphatic dicarboxylic acid such as adipic acid),
an aliphatic diol component (e.g., a C₂₋₁₂ aliphatic diol
such as ethylene glycol, propylene glycol, butanediol, or
neopentyl glycol), and/or a lactone component (e.g., a
25 C₄₋₁₂ lactone such as ϵ -caprolactone), e.g., a poly(ethylene
adipate), a poly(1,4-butylene adipate), and a
poly(1,6-hexane adipate), a poly- ϵ -caprolactone], a

polyether diol [for example, an aliphatic polyether diol, e.g., a poly(oxyC₂₋₄alkylene) glycol such as a polyethylene glycol, a poly(oxytrimethylene) glycol, a polypropylene glycol, or a polytetramethylene ether glycol, and a block
5 copolymer of the poly(oxyalkylene) glycol (e.g., a polyoxyethylene-polyoxypropylene block copolymer); an aromatic polyether diol, e.g., an adduct of an aromatic diol with an alkylene oxide, such as a bisphenol A-alkylene oxide adduct (e.g., an adduct of a C₂₋₄alkylene oxide such
10 as ethylene oxide, or propylene oxide)]; a polyester ether diol (a polyester diol obtained by using the polyether diol as a part of a diol component); and others. The diol(s) may be used singly or in combination. Among these diols, the polyester diol, or the polyether diol such as a
15 polytetramethylene ether glycol (particularly, a polyester diol) is used in many cases.

[0062]

As the chain-extension agent, there may be used a glycol [for example, a short chain glycol, e.g., a
20 C₂₋₁₀alkylenediol such as ethylene glycol, propylene glycol, 1,4-butanediol, or 1,6-hexanediol; bishydroxyethoxybenzene (BHEB)], and in addition a diamine [for example, an aliphatic diamine such as a
C₂₋₁₀alkylenediamine, e.g., ethylenediamine,
25 trimethylenediamine, tetramethylenediamine, or hexamethylenediamine; an alicyclic diamine such as isophorone diamine; an aromatic diamine such as

phenylenediamine, or xylylenediamine]. The chain-extension agent(s) may be used singly or in combination.

[0063]

5 The thermoplastic polyurethane-series resin may also include a perfect thermoplastic polyurethane obtained by using a diol and a diisocyanate at a substantially equivalent amount, in addition an imperfect thermoplastic polyisocyanate having a small amount of a residual free
10 (or unreacted) isocyanate, which is obtained by using a slightly excess amount of a diisocyanate relative to a diol.

[0064]

 Among the thermoplastic polyurethane-series resins, in particular, it is preferred the thermoplastic
15 polyurethane elastomer which is obtained by using a diol (e.g., a diol having a polyester unit or a polyether unit), a diisocyanate, and a glycol (e.g., a short chain glycol) as the chain-extension agent. The thermoplastic polyurethane elastomer comprises a hard segment (hard block)
20 which is composed of a polyurethane with the use of a glycol and a diisocyanate, and a soft segment (soft block) composed of an aliphatic polyether diol (e.g., a poly(oxyethylene) glycol), an aliphatic polyester diol or others. The polyurethane elastomer may include a polyester urethane
25 elastomer, a polyether urethane elastomer, and others, depending on the species of the soft segment.

[0065]

As the thermoplastic polyurethane-series resin, above all, a polyester-polyurethane (particularly a polyester urethane elastomer) obtained by using a polyester diol is preferably used.

5 [0066]

These thermoplastic polyurethane-series resins can be used singly or in combination.

[0067]

In such a range that the effects of the present
10 invention are not deteriorated, the thermoplastic polyurethane-series resin may be used in combination with other resin(s) (e.g., a thermoplastic resin, particularly a thermoplastic elastomer such as a polyamide-series elastomer, a polyester-series elastomer, or a polyolefinic
15 elastomer), a stabilizer (e.g., a heat stabilizer, an ultraviolet ray absorbing agent, an antioxidant), a plasticizer, a lubricant, a filler, a coloring agent, a flame retardant, an antistatic agent, and others.

[0068]

20 In the molded composite article, since the non-urethane-series thermoplastic resin composition contains an amino group, the non-urethane-series thermoplastic resin (composition) firmly joins or bonds with the thermoplastic polyurethane-series resin without
25 using an adhesive. The bonded strength or joined strength of the molded composite article is usually not less than 30 N/cm, and cohesive failure sometimes occurs along with

separation of the resin member formed with the non-urethane-series thermoplastic resin composition (e.g., a hard resin member) from the thermoplastic polyurethane-series resin member (e.g., a soft resin member).

5 The bonded strength of such a molded composite article is usually 30 N/cm to cohesive failure, preferably not less than 40 N/cm, and particularly not less than 50 N/cm (not less than 50 N/cm to cohesive failure).

[0069]

10 The joining may be usually ensured by heating at least one resin selected from the resin composition (the non-urethane-series thermoplastic resin composition) of the present invention and the thermoplastic polyurethane-series resin to be molten, and bringing one
15 resin in the molten state into contact with the other resin. The joining may be conducted by joining the non-urethane-series thermoplastic resin composition with the thermoplastic polyurethane-series resin in a molding process by means of a conventional molding method such as
20 a thermoforming (e.g., a heat press molding, an injection press molding), an injection molding (e.g., an insert injection molding, a two-color (or double) injection molding, a core-back injection molding, a sandwich injection molding), an extrusion molding (e.g., a co-extrusion molding, a T-die
25 lamination molding), or a blow molding.

[0070]

For example, in a molding method such as an insert

injection molding or an injection press molding, the both resin and resin composition may be joined together by heating and melting the thermoplastic polyurethane-series resin, and molding the thermoplastic polyurethane-series resin
5 in a molten state with contacting with at least a part of a resin member composed of the non-urethane-series thermoplastic resin composition (hereinafter, sometimes simply refers as a non-urethane-series resin member). The both resin and resin composition may also be joined together
10 by heating the non-urethane-series thermoplastic resin composition to be molten, and bringing the non-urethane-series thermoplastic resin in the molten state into contact with at least a part of a resin member composed of the thermoplastic polyurethane-series resin
15 (hereinafter, sometimes simply refers as a polyurethane-series resin member). Moreover, in a molding method such as a double injection molding or a co-extrusion molding, joining of the both resin and resin composition may be ensured by heating and melting both the
20 non-urethane-series thermoplastic resin composition and the thermoplastic polyurethane-series resin differently, and molding the molten non-urethane-series thermoplastic resin composition and the molten thermoplastic polyurethane-series resin with contacting with each other.
25 A molded composite article in which the non-urethane-series thermoplastic resin member is firmly joined to the polyurethane-series resin member can be obtained by melting

at least one resin selected from the non-urethane-series thermoplastic resin composition and the polyurethane-series resin, bringing the non-urethane-series thermoplastic resin composition into
5 contact with the thermoplastic polyurethane-series resin for joining, and usually cooling the resulting matter. Moreover, depending on a purpose and an application, it is sufficient to join the non-urethane-series resin member to the thermoplastic polyurethane-series resin member at
10 least in part.

[0071]

Incidentally, the resin or resin composition constituting the resin member (particularly, base resin) can be molten by heating to a temperature of not less than
15 a melting point thereof. In the case of a substantially uncrystallized resin, the resin can be molten by heating to a temperature of not less than a glass transition point (T_g) thereof.

[0072]

20 According to the present invention, since the non-urethane-series thermoplastic resin composition contains an amino group (e.g., an amino group derived from an amino group-containing compound, or an amino group which the resin itself contains) and the amino group acts
25 (chemically acts) on the thermoplastic polyurethane-series resin, the bonded strength can be significantly improved even in a molded composite article obtained from a different

kind of materials, and such a high-level bonded strength cannot be obtained from a physical action caused by simple thermal fusing or welding. Therefore, throughout of this specification, "thermal fusing" includes not only simple
5 thermal fusing, but also thermal fusing (thermal joining) including a chemical reaction.

[0073]

As described above, it is not particularly limited which of the resins between the non-urethane-series
10 thermoplastic resin composition and the polyurethane-series resin is molten. A soft resin (the polyurethane-series resin) having a usually lower melting point or glass transition point (Tg) may be heated, and may be joined to a hard resin member comprising a hard resin
15 (the non-urethane-series thermoplastic resin) having a higher melting point or Tg. Moreover, a hard resin (the non-urethane-series thermoplastic resin composition) having a generally higher melting point or Tg may be heated, and may be joined to a soft resin member comprising a soft
20 resin (the polyurethane-series resin) having a lower melting point or Tg.

[0074]

Among these methods, in particular, the former method has an advantage over conventional techniques since the
25 effects of the present invention are characteristically and effectively exhibited. In the conventional method using simple physical thermal fusing, when letting a

precedently molded non-urethane-series resin member joined with a following molding polyurethane-series resin, the molding temperature of the polyurethane-series resin becomes lower than the melting point of the precedently molded non-urethane-series thermoplastic resin in many cases, and therefore thermal fusing is difficult to proceed. Moreover, even when the molding temperature of the polyurethane-series resin is higher than the melting point of the non-urethane-series thermoplastic resin, the heat quantity is often insufficient to melt the surface of the non-urethane resin member. Therefore, the conventional techniques usually never comprise such a manner as molding the non-urethane-series resin member before molding the polyurethane-series resin. However, according to the present invention, even in such a case, the non-urethane-series resin member and the thermoplastic polyurethane-series resin can be more easily joined together by an action of the amino group contained in the non-urethane-series thermoplastic resin composition. Accordingly, the present invention can increase the freedom of the production process of the composite article and can also rationalize the process step to a large degree.

[0075]

In the molded composite article, although the hard resin usually comprises the non-urethane-series thermoplastic resin composition and the soft resin usually comprises the thermoplastic polyurethane-series resin in

practical cases, the hard resin may comprise the thermoplastic polyurethane-series resin and the soft resin may comprise the non-urethane-series thermoplastic resin. Moreover, the hardness of the non-urethane-series
5 thermoplastic resin composition may be the same level as that of the thermoplastic polyurethane-series resin.

[0076]

To be more precise, in the heat press molding, a molded composite article may be produced by melting at least one
10 resin of the hard resin (or composition) and the soft resin (or composition) in a metal mold of the press molding, bringing the both resins into contact with each other under an applied pressure, and joining the resins to each other. In the heat press molding, the hard resin and/or the soft
15 resin may be filled in the metal mold in a pellet form, a powdered form or other form(s), or may be loaded to the metal mold as a molded article precedently formed by other molding method.

[0077]

20 In the insert injection molding, a molded composite article may be produced by molding any one of the hard resin (or resin composition) or the soft resin (or resin composition) with the use of a molding method (such as an injection molding, an extrusion molding, a sheet molding,
25 or a film molding), inserting or putting thus shaped molded article in a metal mold, and then injecting the other resin to the space or cavity between the molded article and the

metal mold. In the insert injection molding, the molded article to be inserted in the metal mold is preferably pre-heated.

[0078]

5 In the two-color (or double) injection molding, a molded composite article may be produced by injecting any one component of the hard resin (or resin composition) or the soft resin (or resin composition) to a metal mold by means of two injection molding machines or more, and
10 exchanging cavity of the metal mold by rotation or movement of the metal mold, and injecting the other component to the space or cavity between thus obtained molded article and the metal mold.

[0079]

15 In the core-back injection molding, a molded composite article may be produced by injecting any one component of the hard resin (or resin composition) or the soft resin (or resin composition) in a metal mold, enlarging the cavity of the metal mold, and injecting the other component to
20 the space or cavity between thus obtained molded article and the metal mold.

[0080]

 Among these molding methods, particularly from the viewpoint of mass production or other properties, suitable
25 methods are, for example, the heat press molding such as injection press molding, and the injection molding (e.g., insert injection molding, double injection molding,

core-back injection molding, sandwich injection molding).

[0081]

In the thermal fusing, the melting temperature (or thermal fusing temperature) of the hard resin and/or soft resin may be selected depending on the species of the both
5 resins (or resin compositions), and may for example be selected within a range of about 100 to 300°C, preferably about 120 to 290°C, and more preferably about 150 to 280°C. For example, in the heat press molding, the melting
10 temperature may be about 100 to 250°C, preferably about 120 to 230°C, and more preferably about 150 to 220°C. Moreover, in the injection molding, the temperature of the resin in the molding cylinder may for example be about 200 to 300°C, preferably about 220 to 280°C, and more preferably about
15 240 to 280°C.

[0082]

The structure and configuration of the molded composite article is not particularly limited to a specific one, and may be a structure suitable for design, decorative
20 property, touch or others. For example, such a structure may be obtained by coating or laminating a part or all of the soft resin member with the hard resin member, and usually, preferably obtained by coating or laminating a part or all of the hard resin member with the soft resin member (for
25 example, obtained by coating part of the hard resin member, which contacts with human body (such as a hand), with the soft resin member). Moreover, the concrete structure

includes, for example, a two-dimensional structure (such as a sheet-like form, or a plate-like form), and a three-dimensional structure (such as a stick-like form, a tube-like form, a casing, or a housing).

5 [0083]

When the resin composition of the present invention is used, the hard resin and the soft resin can be directly and firmly joined together by thermal fusing without (going through) complicated production steps (e.g., a step for creating a concavo-convex site in the composite area, a step for coating an adhesive). Therefore, the present invention ensures to obtain a lightweight and strong molded composite article improved in properties such as design, decorative property, or good touch or texture (e.g., soft texture, flexibility).

10
15

[Industrial Applicability]

[0084]

The resin composition of the present invention is advantageously used for directly joining or bonding to a thermoplastic polyurethane-series resin to form a molded composite article in which the resin composition is directly joined or bonded to a thermoplastic polyurethane-series resin. Moreover, the obtained molded composite article may be used as various industrial components (or parts), for example, an automotive part (e.g., an automotive interior part such as an instrument panel, a center panel, a center console box, a door trim, a pillar, an assist grip, a steering

20
25

wheel, or an air bag cover; an automotive exterior part such as a lacing, or a bumper; and an automotive functional component such as a rack and pinion boot, a suspension boot, or a constant velocity joint boot), a household electrical part (e.g., a cleaner bumper, a switch of a remote control, 5 and a key top of office automation (OA) apparatus), a product to be used in water (e.g., swimming goggles, and a cover of a underwater camera), an industrial part (a cover part; various industrial parts equipped with a packing for the purpose of sealing property, water proofing property, sound 10 insulating property, vibration insulating property, or other properties; and an industrial rubber roller), an electric or electronic device part (e.g., a curl cord wire covering, a belt, a hose, a tube, and a sound deadening gear), sports goods, shoes goods (e.g., athletic shoes, 15 a shoe sole), and a part requiring design or decorative property (e.g., dark glasses and glasses).

[0085]

Among them, the molded composite article is particularly suitable for a constitutive member of the shoe 20 or the roll (e.g., a rubber roller). The constitutive member of the shoe includes a shoe part such as a shoe sole (sole), or a shoe upper, and others. Moreover, the molded composite article may form (or constitute) athletic shoes, work shoes 25 (e.g., boots, rain shoes, shoes for gardening). In such a shoe application, since a combination of a hard or glass fiber-reinforced polyamide-series resin and a soft

polyurethane-series resin, which was difficult in the past,
becomes easy, it is, for example, possible to compound
different grades of materials in many layers. Accordingly,
the molded composite article greatly contributes to
5 improvement in design or functionality of the shoe.

[0086]

Further, in the roll (e.g., a rubber roller)
application, for example, the roll may comprise an axis
(shaft) in which at least the surface layer comprises a
10 non-urethane-series thermoplastic resin (composition),
and a thermoplastic polyurethane-series resin layer formed
along the surrounding surface of the axis. The axis may
be obtained by forming a non-urethane-series thermoplastic
resin layer on the surface of the metal shaft, or may be
15 an axis comprising a non-urethane-series thermoplastic
resin. In such a roller application, since a cutting finish
for obtaining a shaft precision and a surface finish of
a thermoplastic polyurethane-series resin can be conducted
in one operation by the same grinding machine, the production
20 process of the roller can be significantly abbreviated and
the cost can be exponentially reduced. Moreover, since such
a roller given by chemically joining has high bonded strength
and merely has the space or cavity between the axis and
the roll, the roller can tolerate the usage in a high torque.

25 [Examples]

[0087]

The following examples are intended to describe this

invention in further detail and should by no means be interpreted as defining the scope of the invention.

[0088]

Examples 1 to 7 and Comparative Example 1

5 (1) Preparation of non-urethane-series thermoplastic resin composition

(i) To 100 parts by weight of a polyamide 12 (number average molecular weight: 19,000, amino group concentration: 8 mmol/kg), was added 5 parts by weight of
10 a polyamide 12 oligomer (number average molecular weight: 3,000, amino group concentration: 530 mmol/kg), the resultant was mixed with a biaxial extruder to obtain a non-urethane-series thermoplastic resin (A1) (amino group concentration: 20 mmol/kg).

15 [0089]

(ii) A non-urethane-series thermoplastic resin (A2) (amino group concentration: 40 mmol/kg) was obtained in the same manner with the above (i) except that hexamethylenediamine (0.5 parts by weight) was used instead
20 of the polyamide 12 oligomer.

[0090]

(iii) Non-urethane-series thermoplastic resin (A3) (amino group concentration: 100 mmol/kg) was obtained in the same manner with the above (i) except that amino
25 group-modified polyether (Sanamyl TAP-10, manufactured by Sanyo Chemical Industries, Ltd.) (5 parts by weight) was used instead of the polyamide 12 oligomer.

[0091]

(iv) Non-urethane-series thermoplastic resin (A4) (amino group concentration: 35 mmol/kg) was obtained in the same manner with the above (i) except that polyamide
5 6 (number average molecular weight: 23,000, amino group concentration: 17 mmol/kg) (100 parts by weight) was used instead of the polyamide 12.

[0092]

(v) To a polyester elastomer (Hytrel, manufactured
10 by DU PONT-TORAY CO., LTD) (100 parts by weight), was added a polyamide 12 oligomer (number average molecular weight: 3,000, amino group concentration: 530 mmol/kg) (5 parts by weight), the resultant was mixed with a biaxial extruder to obtain a non-urethane-series thermoplastic resin (A5)
15 (amino group concentration: 15 mmol/kg).

[0093]

(vi) A non-urethane-series thermoplastic resin (A6) (amino group concentration: 15 mmol/kg) was obtained in the same manner with the above (v) except that a polycarbonate
20 (Iupilon, manufactured by Mitsubishi Engineering-Plastics Corporation) (100 parts by weight) was used instead of the polyester elastomer.

[0094]

(vii) A non-urethane-series thermoplastic resin (A7)
25 (amino group concentration: 15 mmol/kg) was obtained in the same manner with the above (v) except that a polyphenylene sulfide (Fortron, manufactured by Polyplastics Co. Ltd.)

(100 parts by weight) was used instead of the polyester elastomer.

[0095]

(viii) As a comparison, a polyamide 12 having an amino
5 group concentration of 5 mmol/kg was singly used
(non-urethane-series thermoplastic resin (A8)).

[0096]

(2) Production of molded composite article and peeling
test thereof

10 With an ester-series thermoplastic polyurethane
elastomer TPU (ET195, manufactured by BASF), a flat plate
having 120 mm width, 25 mm long and 2 mm thick was produced
with an injection molding machine. The flat plate was placed
in a metal mold for injection molding having 120 mm width,
15 25 mm long and 4 mm thick, and injection molding of the
non-urethane-series thermoplastic resin or resin
composition obtained in the above (1) was carried out under
a condition of a joining temperature (cylinder temperature)
of 250°C and a metal mold temperature of 60°C to obtain a
20 molded composite article.

[0097]

Thus obtained molded composite articles were cut to
a piece having 100 mm length and 20 mm width. The part covered
with aluminum foil was used as a tong hold, and the tensile
25 test was conducted by drawing the tong hold to 180° direction
at a drawn speed of 20 mm/minute. Through the tensile test,
the peel strength in the fusing interface between the

non-urethane-series thermoplastic resin member and the urethane-series thermoplastic resin member was measured. On the basis of the peel strength, the thermal fusing property between the resin members was evaluated.

5 [0098]

The results are shown in Table 1.

[0099]

[Table 1]

Table 1

	Non-urethane-series thermoplastic resin	Amino group concentration mmol/kg	Peel strength N/cm
Example 1	A1	20	130
Example 2	A2	40	110
Example 3	A3	100	130
Example 4	A4	35	110
Example 5	A5	15	80
Example 6	A6	15	70
Example 7	A7	15	80
Comparative Example 1	A8	5	30

[Document Name] Abstract

[Abstract]

[Object(s)] To provide a non-urethane-series thermoplastic resin composition directly and firmly joinable to a thermoplastic polyurethane-series resin member even if a base resin is a non-urethane-series thermoplastic resin.

[Means to Solve the Problems] A resin composition directly joinable to a thermoplastic urethane-series resin comprises a non-urethane-series thermoplastic resin (e.g., a polyamide-series resin, a polyester-series resin, a polycarbonate-series resin, and a polyphenylene sulfide-series resin), and an amino group-containing compound (e.g., a polyamide oligomer). The resin composition may contain an amino group in a concentration of not less than 10 mmol/kg. The amino group-containing compound may have an amino group in a concentration of 40 to 1000 mmol/kg. The proportion of the amino group-containing compound may be about 0.01 to 20 parts by weight relative to 100 parts by weight of the non-urethane-series thermoplastic resin.

[Selected Fig.] none

Applicant Record

	Identification No.	[000108982]
	1. Date of Alternation	July 12, 2001
5	[Reason of Alternation]	change of name
	Address	2-5, Kasumigaseki 3-chome, Chiyoda-ku, Tokyo
	Name	Daicel-Degussa, Ltd.
	2. Date of Alternation	May 11, 2004
10	[Reason of Alternation]	change of address
	Address	18-1, Konan 2-chome, Minato-ku, Tokyo
	Name	Daicel-Degussa, Ltd.